Adsorption Mechanism of a Cationic Surfactant on Textiles in Excess Anionic Surfactant Solution

Shigeru Yanaba*, **Hirofumi Kanao** and **Osamu Okumura**
Development Laboratories II, Lion Corp., No. 13-12, 7-chome, Hirai, Edogawa-ku, Tokyo, 132 Japan

The present study was carried out to clarify the adsorption mechanism of a cationic surfactant (dihydrogenated tallow dimethyl ammonium chloride (DHTDMAC) onto various fibers in excess of anionic surfactant solutions. Actually, in such a solution, DHTDMAC becomes an anionic/cationic complex and comes into contact with fibers through the physical force of mechanical stirring. At that time, adsorption of the complex onto textile depends on the extent of the work of adhesion (WA). In fact, WA and amounts of DHTDMAC adsorbed onto fibers were correlated very closely. Furthermore, the difference of WA according to the complex is discussed. Two hypotheses are presented. One is based on differences arising from the hydrophobic character of the complex itself. The other is based on the manner in which the anionic surfactant and cationic surfactant are situated in the complex molecule. The WA of the complex is explained on the basis of these hypotheses.

Many studies have been carried out on the mechanism of adsorption of anionic or cationic surfactants on textiles. The use of cationic and anionic surfactants in combination also has been reported. In such a case, the cationic surfactant is treated as a dispersion and when used with excess anionic surfactant solution, it is not adsorbed onto textiles. In the previous paper (1), we found that, if a cationic surfactant is used as a corpuscle (fine solid, over 10 μm) in excess anionics, adsorption onto various textiles becomes possible. To gain some understanding of this phenomenon, the work of adhesion (WA) between the sodium linear alkyl benzene sulfonate (LAS)/DHTDMAC complex and the surface of a textile was calculated by Wu's equation (2), measuring the contact angle of two liquids with the complex (3). Finally WA and the amounts of cationic surfactant adsorbed onto textiles were found to be very closely correlated.

The present investigation was carried out to extend this theory to other types of anionic surfactants, sodium alpha olefin sulfonate (AOS), sodium alkyl sulfate (AS) and sodium alkyl ethoxy sulfate (AES). The hydrophobic character and structure of each complex are discussed.

EXPERIMENTAL

Materials. DHTDMAC (average mol wt 563.5) was prepared by drying Arqurd 2HT (Lion Akzo Co., Tokyo, Japan), salting out inorganic substances by dissolution of it in benzene, and recrystallization from acetone. Refined DHTDMAC was granulated in a mortar and divided into 250–149 μm, 105–63 μm and under 44 μm using a standard sieve. Average particle size was determined by scanning electron microscopy. It was difficult to obtain a DHTDMAC particle less than one μm in size. Thus, the DHTDMAC particles less than 40 μm were added to water and dispersed with a homogenizer (Polytron, Kinematica Co., Luzern, Switzerland) or ultrasonic (UTS-45 NP type, Huso Industry Co., Osaka, Japan) to obtain a particle range of 0.1–0.6 and 0.1–0.3 μm. The average particle size was determined by using membrane filters (Millipore Co., Massachusetts) of different pore size (Table 1).

The concentration of DHTDMAC tested was 53 ppm in each case. The concentrations of LAS (average mol wt 345.5, C_{11}-C_{13}), AOS (351, C_{14}-C_{18}), AS (288, C_{12}-C_{14}), AES (436, C_{13}, 3EO) were all 276 ppm. Zeolite 4A type (Silton B, Mizusawa Co., Tokyo, Japan) and sodium silicate JIS 1st. grade (Japan Chem. Co., Tokyo, Japan) were used. Each concentration was 200 and 135 ppm. Sodium carbonate and sodium sulfonate were of the reagent grade. The concentrations were 135 and 600 ppm.

16DMS [16-Doxyl (4,4-dimethyloxazolidine-N-oxyl)-stearic acid methyl ester] and TEMPO [4-Hydoxy-TEMPO (2,2,6,6-tetramethylpiperidine-N-oxyl)] were used as ESR spin labels.

Textiles. Cellulose (knitted cotton), 6-nylon (tricot) and polyester (jersey) were cut into 5- × 5-cm pieces and were refined by extracting a surfactant and other textile treatments. For this purpose, Soxtec HT2 (Tecator Co., Höganäs, Sweden) was used. Those textiles were refluxed in $CHCl_3/C_2H_5OH$ 1/1 for 30 min and rinsed for 50 min, and the solvent was removed.

Analysis of DHTDMAC adsorbed on textiles. All the textiles (30 g) were treated with 900 ml of a test solution (25 C, 3 DH) and cationic surfactant corpuscles using Terg-O-Tometer (120 rpm and 10 min). They were air dried for two days and DHTDMAC was extracted by $CHCl_3/CH_3CH_2OH$ 1/1 using Soxtec HT2, possibly in the complex form. The extract was analyzed by high performance liquid chromatography (HPLC). The HPLC used was Shimazu LC-3A. The column was NUCLEOSIL 5SA for DHTDMAC and NUCLEOSIL 5SB for the anionic surfactants. The mobile phase was $NaClO_4/CH_3OH$ and the detector was RI.

Measurement of contact angle. The same molar ratio solution of each anionic surfactant (LAS, AOS, AES and AS) and DHTDMAC was mixed, followed by filtering the insoluble matter, washing by water and drying under reduced pressure. The molar ratio of anionic surfactant and DHTDMAC in the complex was analyzed by HPLC and found to be from 1.00 to 1.04.

TABLE 1

Average Particle Size of DHTDMAC

	Particle size distribution (μm)	Average particle size (μm)
Dispersed	0.1–0.3	0.15
	0.1–0.6	0.35
Solid	1–44	22
	63–105	76
	149–250	205

---

*To whom correspondence should be addressed.

The complex was melted, spread over a glass plate and allowed to solidify. The melted temperature was 166.4 C for the LAS/DHTDMAC complex, 123.0 C for AS/DHTDMAC, 71.0 C for AOS/DHTDMAC and 63 C for AES/DHTDMAC. The plate was then placed for two days in saturated water or methylene iodide vapor. The contact angle was determined by Equation [1] using the height (h) and radius (r) of a droplet of water and methylene iodide on the solidified complex. An Erma contact anglemeter (Goniometer type; Model G-1) was used.

$$\tan \theta/2 = h/r \qquad [1]$$

X ray, ESR analysis. Rigaku Geigerflex (30 KV, 10 mA) was used for the X ray analysis that was measured from $2\theta = 0.5$ to 30. X ray analysis was carried out for all complexes before and after melting. They showed the same patterns. That is, the change in the crystal form was not detected for any of the complexes due to melting.

A JES-FE1X type spectrometer (Nihon Denshi Co., Tokyo, Japan) was used for ESR analysis, and the aN′ value was determined by Equation [2].

$$aN' = 1/3\,(2A\perp + A/\!/) \qquad [2]$$

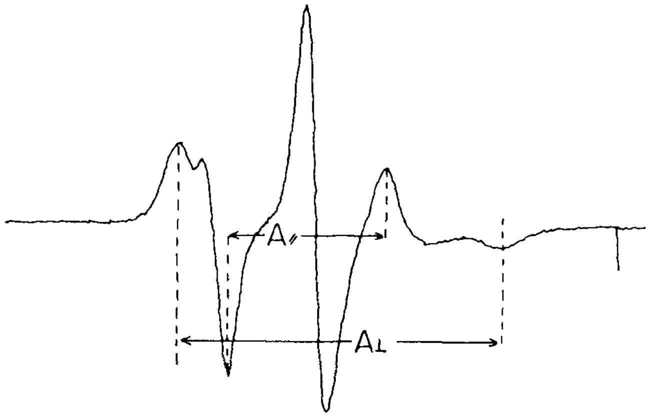

FIG. 1. ESR spectrum of anisotropic state.

RESULTS AND DISCUSSION

Adsorption of the complex on textiles. When DHTDMAC particles of different size were added to an anionic surfactant solution, adsorption failed to occur for a size less than one μm but did so beyond 10 μm on all textiles (Figs. 2-4). The amounts of DHTDMAC adsorbed onto polyester and nylon was more than that adsorbed on cotton. Of the anionic surfactants, LAS was adsorbed the most. The order of DHTDMAC adsorption was LAS>AS>AOS>AES for all textiles.

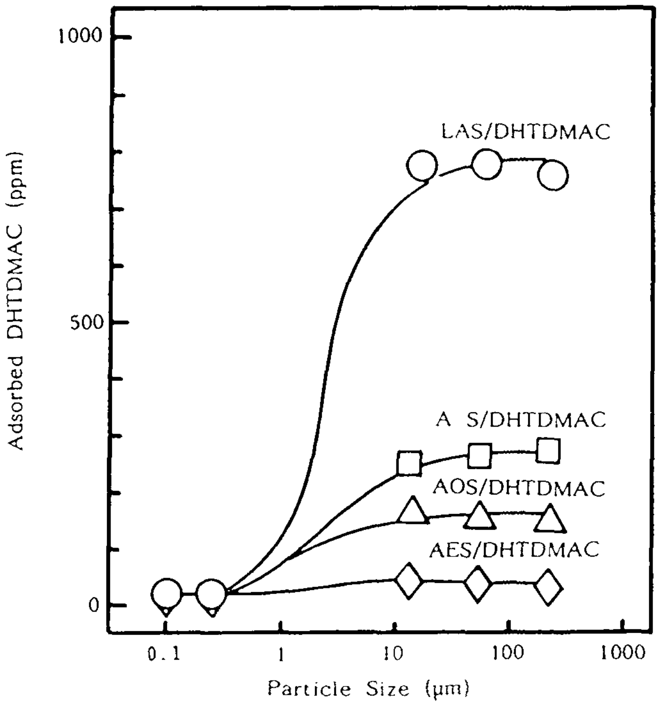

FIG. 2. Adsorption of DHTDMAC on polyester in various anionics.

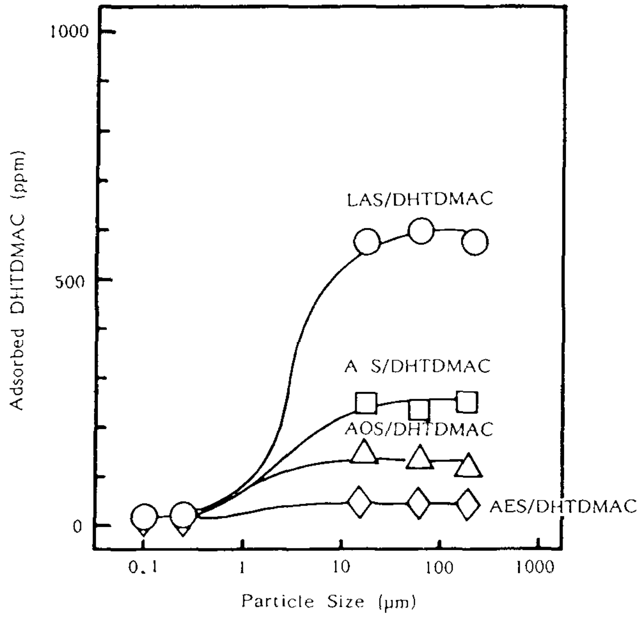

FIG. 3. Adsorption of DHTDMAC on nylon in various anionics.

Formation of an anion/cation complex. As a cationic surfactant corpuscle is added to the excess anionic solution, the complex can be made immediately on the surface of the corpuscle by an ionic reaction. To examine the formation of the complex, the test solution and cationic surfactant corpuscles (average particle size, 205 μm) were stirred in the Terg-O-Tometer for 10 min without textiles. The residue was filtrated, washed by water to remove any deposited anionics and dissolved in chloroform. The remaining unreacted cationic surfactants were qualitatively analyzed by 4′,5′-dichlorofluorescein. However, no cationic character was detected. All cationic surfactants are changed to the complex.

Deposition of a complex onto textiles can be treated by the WA between them in the solution. For the first step of reaction time, namely two or three min afterwards, there will be unreacted cationic surfactants.

TABLE 2

Contact Angles of Water and Methylene Iodide With the Complex

	LAS/DHTDMAC	A S/DHTDMAC	AOS/DHTDMAC	AES/DHTDMAC
Water	101.0°	75.0	55.1	40.1
Methylene iodide	54.8	65.9	66.7	52.4

However, the whole surface of the cationic surfactant corpuscles should be covered with the complex, so that we could use WA in this case.

Work of adhesion (WA) of the complex. The WA is defined as the energy difference of a surface which disappeared by adsorption of a complex onto a textile in solution (in this case, the surface of the complex-solution and textile-solution) and a surface generated by adsorption (in this case, the surface of the complex-textile). WA is expressed by Equation [3].

$$WA = (\gamma_{CW} + \gamma_{TW}) - \gamma_{CT} \qquad [3]$$

The interfacial tension of Equation [3] exists between liquid and solid or solid and solid and thus cannot be determined directly by experiments. So, using Equation [5] previously reported (1), derived from Equation [4], Wu's equation, the WA was calculated, substituting known values of water and methylene iodide surface tension and the observed values of contact angle between the two liquids and the complex.

$$\gamma_{LS} = \gamma_L + \gamma_S - (4\gamma_L{}^d \times \gamma_S{}^d)/(\gamma_L{}^d + \gamma_S{}^d)$$
$$- (4\gamma_L{}^p \times \gamma_S{}^p)/(\gamma_L{}^p + \gamma_S{}^p) \qquad [4]$$

$$\gamma_L(1 + \cos\theta) = (4\gamma_L{}^d \times \gamma_S{}^d)/(\gamma_L{}^d + \gamma_S{}^p)$$
$$+ (4\gamma_L{}^p \times \gamma_S{}^p)/(\gamma_L{}^p + \gamma_S{}^p) \qquad [5]$$

This contact angle is shown in Table 2 and the work of adhesion in Table 3.

The WA was found to decrease in the order LAS>AS>AOS>AES, as was the case for DHTDMAC adsorbed onto the textiles. In Figure 5, the amounts of adsorbed DHTDMAC on all the textiles are plotted vs the WA. A very close correlation was indicated (correlation coefficient was 0.964). Thus, adsorption can be explained on the basis of the WA, not only in the case of LAS but also for AOS, AES and AS.

Differences in the WA for the anionic surfactants are discussed below.

TABLE 3

Work of Adhesion of Each Complex

Complex	Fiber[a]	γ_{CT}	γ_{TW}	γ_{CW}	WA
LAS/DHTDMAC	Cellulose	33.6	1.4	43.3	11.1
	Nylon	10.3	18.1	43.3	51.1
	Polyester	1.6	40.3	43.3	82.0
AOS/DHTDMAC	Cellulose	1.6	1.4	5.9	5.8
	Nylon	14.4	18.1	5.9	9.7
	Polyester	35.9	40.3	5.9	10.3
AES/DHTDMAC	Cellulose	0.3	1.4	2.0	3.1
	Nylon	15.1	18.1	2.0	5.0
	Polyester	37.7	40.3	2.0	5.0
AS/DHTDMAC	Cellulose	6.5	1.4	14.9	9.9
	Nylon	18.1	18.1	14.9	27.4
	Polyester	20.0	40.3	14.9	35.3

[a]Value of γ_{TW} for cellulose and polyester (4); for nylon (5).

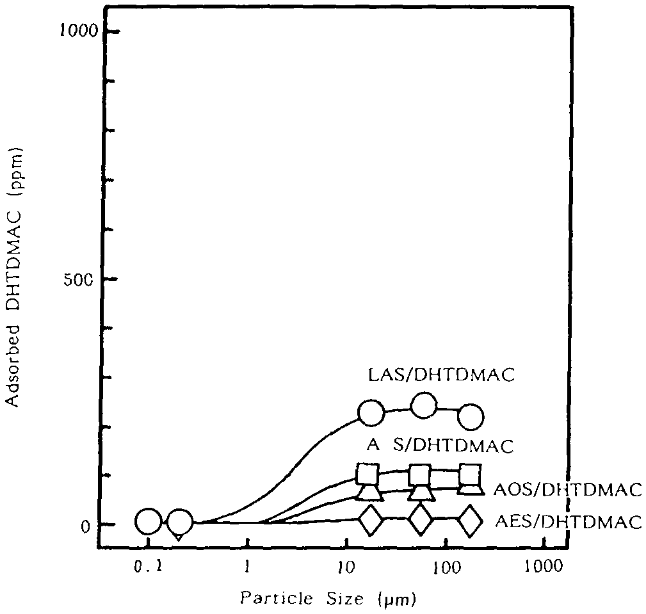

FIG. 4. Adsorption of DHTDMAC on cotton in various anionics.

Hypothesis for differences in work of adhesion (WA). In Table 4, the surface tension of four complexes is shown. For the AOS, AS and AES complexes, γ^d is smaller than γ^p, but γ^d is greater than γ^p in LAS. The relation between γ^d and γ^p in the LAS complex is essentially the same as that in the solid surface tension of paraffin. Thus, why should the LAS/DHTDMAC complex show a paraffin-like character? Two hypotheses are proposed for this. One is that the hydrophobic character originates from polarity of the complex itself. The other is that the anionic surfactant molecule and DHTDMAC molecule are arranged differently in the complex molecule. The former was evaluated by the ESR spectrum of the spin label method and the latter by the X ray scattering spectrum.

Determination of the complex polarity by ESR. The spin label was added to the test sample, and limited circumstance near the spin label was discussed from its

TABLE 4

Surface Tension of the Complex and Paraffin

	LAS/DHTDMAC	AOS/DHTDMAC	A S/DHTDMAC	AES/DHTDMAC	Paraffin (3)
γ	29.4	47.6	33.8	57.7	24.8
γ^d	27.7	13.0	14.5	17.4	24.8
γ^p	1.6	34.5	19.3	40.2	0

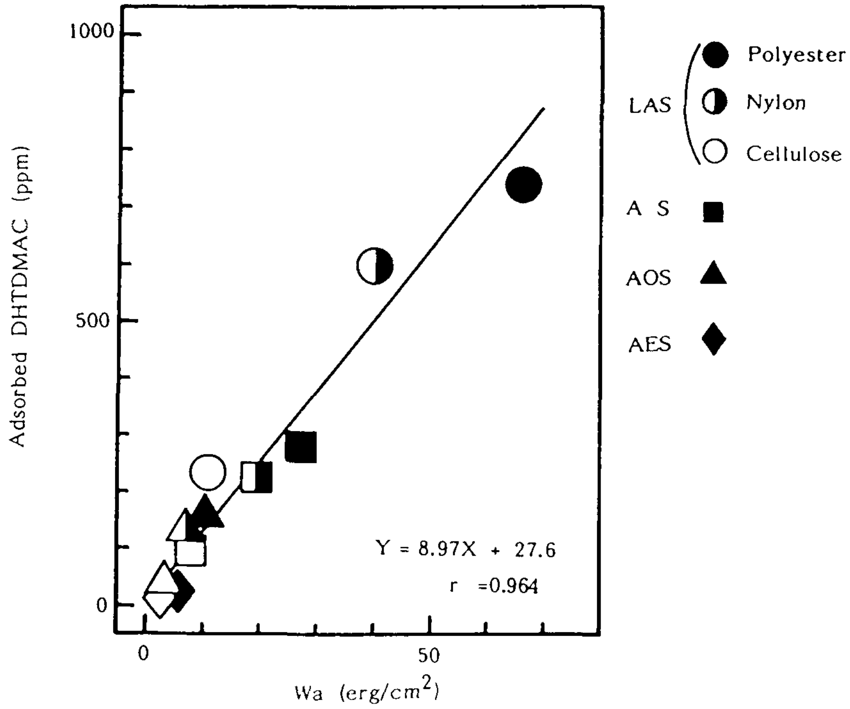

FIG. 5. Correlation between amounts of adsorbed DHTDMAC on textiles and WA.

spectrum. 16DMS was used as the hydrophobic spin label and TEMPO as the hydrophilic spin label. 16DMS may enter the alkyl chain and provide information on its polarity, and TEMPO, information on the near polar group. A spectrum of ESR is usually composed of three peaks, and the distance between the outer peaks provides an indication of polarity. Half of this distance is called the aN value, which is maximum in water and minimum in paraffin. For an ordinary substance, that is between these. In this study, the ESR spectrum showed anisotropy and thus the aN′ and not the aN value was used.

The aN′ values of LAS, AOS, AES and AS complex and amounts of adsorbed DHTDMAC are shown in Figure 6. aN′ increased in the order AS>LAS>AOS>AES in both 16DMS and TEMPO. The amounts of adsorbed DHTDMAC increased in the order AS>AOS>AES, except LAS. For the former three anionics, the higher the hydrophobic character of the complex, the greater was the degree of adsorption. But we cannot explain results for LAS using this hypothesis.

Determination of surfactant molecule arrangement in the complex by X ray analysis. The X ray spectrum

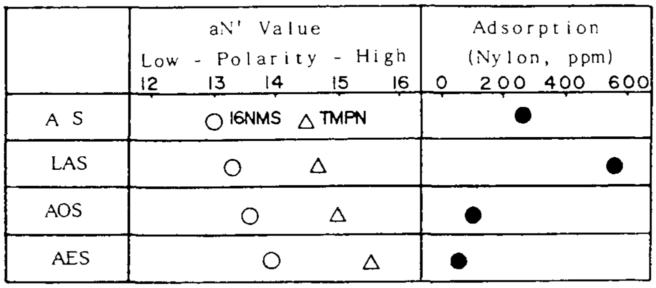

FIG. 6. Correlation between amounts of adsorbed DHTDMAC and aN′.

TABLE 5

Long and Short Spacings of the Complex

	Long spacing (A)	Short spacing (A)
DHTDMAC	34	4.7, 4.3, 3.9
LAS/DHTDMAC	25	4.7
A S/DHTDMAC	46	4.3
AOS/DHTDMAC	49	4.2
AES/DHTDMAC	41	4.3

of DHTDMAC is shown in Figure 7a. DHTDMAC is known to form a layer structure (Fig. 8). Thus, in Figure 7a, 2θ = 18.7, 20.8 and 22.5 are assigned to short spacings (the distances being 4.7, 4.3 and 3.9 A) and 2θ = 1.5 to a long spacing (34 A). In Figure 7b, the spectrum of the AOS/DHTDMAC complex is shown. All short and long spacings are shown in Table 5. In a short spacing pattern, DHTDMAC has three peaks, meaning that the crystal is rhombic. But in the case of the complex, a single peak was shown, implying that the crystal changes to a cubic shape. All long spacings expanded except that for the LAS/DHTDMAC complex. In this case, the LAS/DHTDMAC complex may have a specific arrangement compared to the others. To explain why the LAS/DHTDMAC complex has a paraffin-like hydrophobic character and why its long spacing becomes shorter than that of DHTDMAC, we proposed the model of molecule arrangement shown in Figure 8.

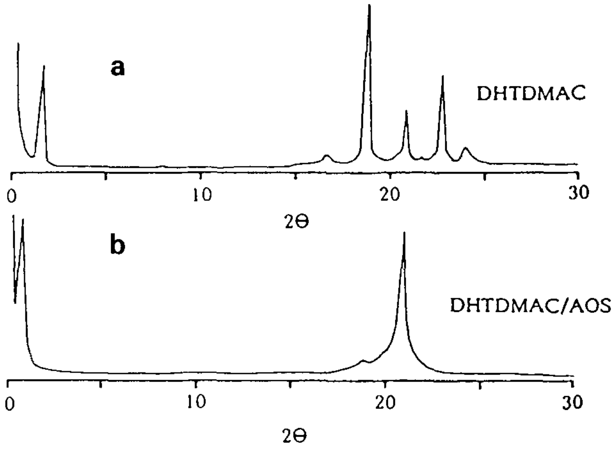

FIG. 7. X ray spectrum of DHTDMAC and the DHTDMAC/AOS complex.

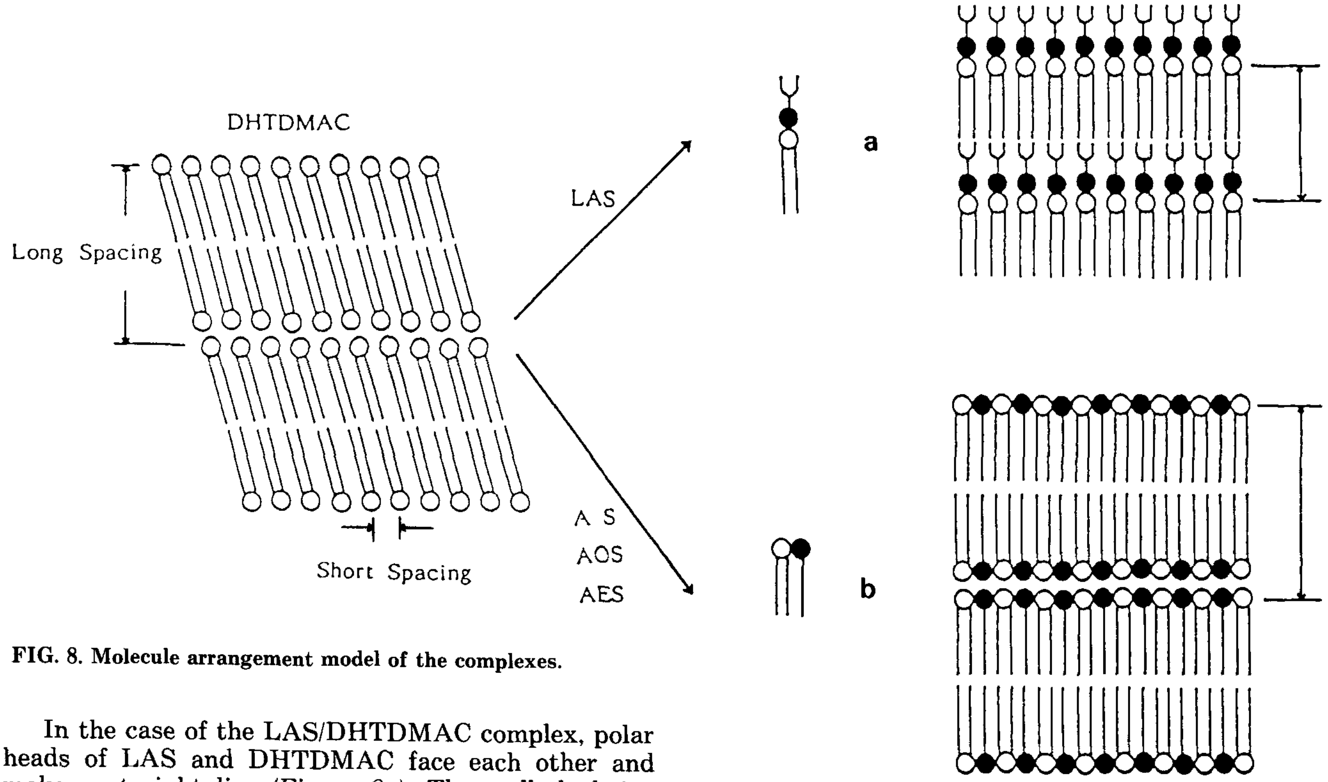

FIG. 8. Molecule arrangement model of the complexes.

In the case of the LAS/DHTDMAC complex, polar heads of LAS and DHTDMAC face each other and make a straight line (Figure 8a). Thus, alkyl chains always face to the outside surface and should show a paraffin-like character, and long spacing will become shorter than that of DHTDMAC.

In the case of another anionic surfactant, the polar heads and alkyl chains formed parallel bars (Figure 8b), thus indicating long spacings to increase from 34 A to 41–49 A. Because the actual surface of this complex is formed by polar head or alkyl chain blocks, its hydrophobic character will decrease more than that of LAS/DHTDMAC.

These differences in molecular arrangement should be due to the fact that in the case of LAS and DHTDMAC, there is a strong steric hindrance between LAS alkyl and DHTDMAC alkyl chains, but little between those of straight alkyl (AOS, AES, AS) and DHTDMAC.

REFERENCES

1. Okumura, O., H. Kanao, S. Yanaba and K. Kiyama, *Yukagaku 36*:38 (1987).
2. Wu, S., *J. Macromol. Sci. Revs. Macromol. Chem. C10(1)*:1 (1974).
3. Saito, M., M. Hayasi and A. Yabe, *Yukagaku 28*:328 (1979).
4. Saito, M., M. Otani and A. Yabe, *Textile Res. J. 55*:157 (1985).
5. Yabe, A., N. Yoshizumi, K. Sekine and M. Saito, Annual Meeting of the Society of Fiber Science and Technology, Japan, 1980, p. 87.

[Received January 4, 1988;
accepted July 6, 1988]